

Chemical Effects of I. T. ^{95m}Tc - ^{95g}Tc in some Pertechnetates in Aqueous Solution

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(Received October 23, 1980; revised February 16, 1981)

Isomeric transition / Technetium / Pertechnetate / Chemical effects

Abstract

Although the distribution of ^{95g}Tc amongst the different products following isomeric transition in solid samples of pertechnetates is independent of the pH of the solution in which the dissolution for analysis takes place, the same is not true if the decay takes place in solution. The ^{95g}Tc appears in neutral and cationic forms as well as TcO_4^- and another anionic species. Introduction of scavengers into the solution suggests that this pH effect may arise from reactions of the primary ^{95g}Tc products with radiolytic products formed in the solution by Auger electrons released during the isomeric transition.

1. Introduction

The high retention following isomeric transition in solid pertechnetates labelled with ^{95m}Tc [1] suggests an investigation of the effects in aqueous solution, where the crystal cage effect is absent. Although few data are available on similar systems, there are indications of other factors complicating the interpretation of results. For instance, HILLMAN has found that the distribution of the ground state between the tetra- and hexavalent chemical species, following decay of the tellurium isomers, is dependent on the pH of the solution in which decay takes place [2]. The yield of hexavalent ground state species increased with the pH of the solution. Isomeric transition in selenates has also been reported to give a pH-dependent distribution of ground state species [3]. An unusual feature of the selenate results was that solutions of the lithium salt behaved differently from the solutions of the sodium, potassium or caesium salts.

The only other system in which radioactive decay leads to a pH-dependent distribution of the products seems to be the β^- decay of Ce and Yb in complexes and this has been attributed to a pH-dependent decomposition of the excited complex [4].

It should be noted that retention following (n, γ) in perhenate solutions is close to 100% [5].

2. Experimental

2.1. Preparation of $^{95m}\text{TcO}_4^-$ solution

The ^{95m}Tc was obtained by the reaction $^{96}\text{Mo}(p, 2n)^{95m}\text{Tc}$ on natural molybdenum powder, using 20 MeV protons from the SIN cyclotron at Villigen, Switzerland. The target was stored for about 2 months before proces-

sing, during which time the primary ^{95g}Tc (20 h) and ^{96}Tc (4 d) decay.

The target was dissolved in peroxide to give a solution of pertechnetate, as described previously [6]. The ^{95m}Tc was separated by extraction with methyl-ethyl-ketone after adjusting the pH of the solution to 8 with a small quantity of lithium, potassium or ammonium hydroxide solution, depending on the salt to be investigated. The extract was dried in vacuo.

2.2. Preparation of the labelled pertechnetate

$\text{Li}^{99}\text{TcO}_4$ and $\text{K}^{99}\text{TcO}_4$ were prepared by dissolving hydrated $^{99}\text{TcO}_2$ in 3% hydrogen peroxide and refluxing to destroy the excess of peroxide. The pertechnetic acid was then neutralized with lithium or potassium hydroxide solutions, the end point being deduced from potentiometric measurements of the pH. For the ammonium salt, a few drops of hydrogen peroxide were added to the original ammoniacal solution of pertechnetate, supplied by the Radiochemical Centre, Amersham, and the mixture evaporated until the excess peroxide was destroyed. Solutions of $\text{Li}^{99}\text{TcO}_4$, $\text{K}^{99}\text{TcO}_4$ and $\text{NH}_4^{99}\text{TcO}_4$ were then mixed with solutions of the corresponding salt of $^{95m}\text{TcO}_4^-$ and aliquots of the mixtures evaporated to dryness under reduced pressure. The ^{95m}Tc -labelled pertechnetates were then dissolved in solutions, adjusted to the required pH, saturated with nitrogen and stored at 3 °C to reach the transient equilibrium of the $^{95m}\text{Tc}/^{95g}\text{Tc}$ isomeric pair.

2.3. Tc(IV) carrier solutions

One carrier solution was prepared by the dissolution of freshly prepared hydrated TcO_2 in sulphuric acid [1] followed by adjustment of the pH to the desired value by the appropriate alkali hydroxide (Carrier A).

At pH > 2 some technetium reprecipitated and after centrifugation the residual solution contained only traces of technetium. For the higher pH values, another carrier solution was used. It was prepared by the hydrolysis of $(\text{NH}_4)_2\text{TcCl}_6$ in an acetate buffer solution (Carrier B) [7].

Above pH 5, some technetium precipitated from these latter solutions. It was separated by centrifugation and the supernatant solution, which was used as carrier, contained less than 10^{-4} M Tc(IV).

These carrier solutions were investigated by electrophoresis using a previously described procedure [7]. The sulphuric

acid solution (Carrier A) at pH 0.1 contained only an uncharged species. At pH 1.7, a small amount of a cationic species appeared. The other carrier solutions also contained a cationic and neutral species, the proportion of the former decreasing at higher pH values.

2.4. Solutions used in investigation

Labelled pertechnetate solutions of appropriate pH were prepared as above. With the exception of the experiments conducted at pH > 8, a small quantity of carrier solution was added. After the experiments yielding the data of Figure 1, for which both carrier solutions were tried, solution A was used for experiments at pH ≤ 1.7 and solution B up to pH 8. The final concentration of technetium was about $8 \cdot 10^{-3}$ M and the volume 200 μ l.

2.5. Separation procedure

After establishment of transient equilibrium in the solutions stored at 3°C, the different technetium species were separated by low voltage electrophoresis. In a few experiments, the less selective solvent extraction separation was tried. The paper strips for electrophoresis were Schleicher-Schull No 2043 B and the supporting electrolyte was 1 M H₂SO₄. A voltage of 400 V was applied for 1 1/2 hours. From the original 200 μ l solution, more than half was used for electrophoretic runs and the rest was diluted to 5 ml with 3 M H₂SO₄ and the TcO₄⁻ extracted by isoamyl alcohol.

2.6. Measurement of ^{95g}Tc

The activity of ^{95g}Tc in the different fractions was determined using a high resolution Ge/Li detector and pulse analysis selection of the 766 keV emission [6].

3. Results

Figure 1 shows that carriers A and B give only slightly different results, the difference being greatest at pH ~5. The proportion of ^{95g}TcO₄⁻ is lower for the solution containing the carrier prepared by the hydrolysis of (NH₄)₂TcCl₆ in acetate solution.

Previous work (Ref. [7] and unpublished) has shown that in the absence of carriers, trace amounts of Tc(IV) species are liable to aerial oxidation, so that, as far as possible, an attempt was made to avoid such conditions. At both low and high pH, in the absence of carrier, more than 90% of the ^{95g}Tc is found as TcO₄⁻. Between pH 3 and 5 somewhat more separable ^{95g}Tc is found, but all the results obtained under these conditions show poor reproducibility.

The influence of pH on the distribution of ^{95g}Tc in LiTcO₄ solution is presented in Figure 2. The yield of ^{95g}TcO₄⁻ decreases from 90% at pH 0.1 to about 40% at pH ~3,

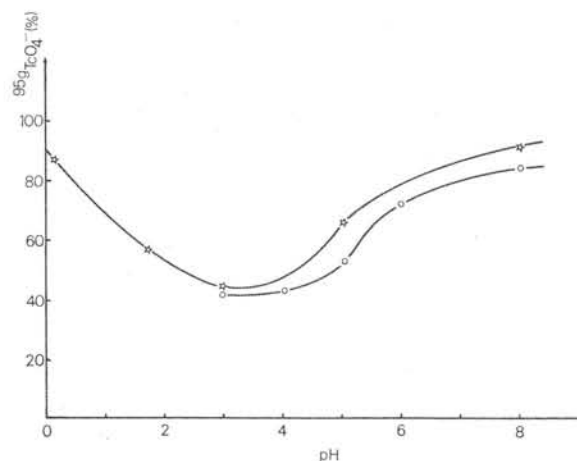


Fig. 1. Yield of ^{95g}TcO₄⁻ vs. pH in LiTcO₄ solution
☆ carrier A; ○ carrier B

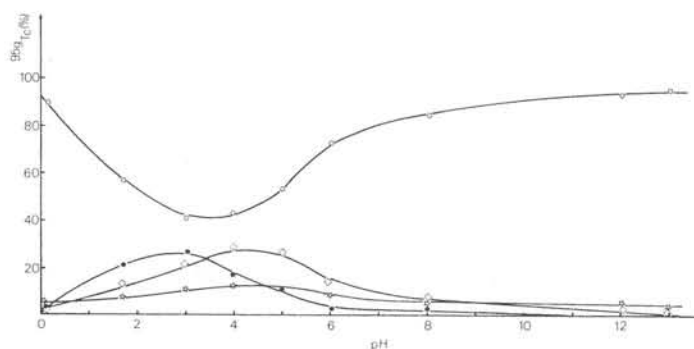


Fig. 2. Influence of pH on the chemical distribution of ^{95g}Tc in LiTcO₄ solution in the presence of Tc(IV) carrier, carrier A at pH < 1.7, carrier B at 1.7 > pH < 8. ○ retention, ● cation, ◇ uncharged species, ☆ anion

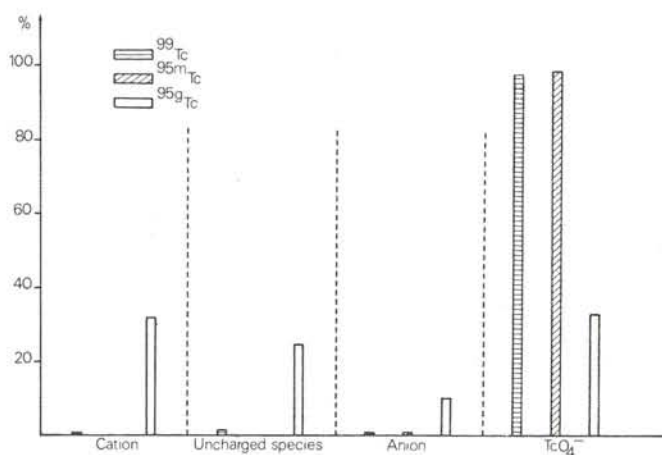


Fig. 3. Distribution of Tc in different chemical species in the LiTcO₄ solution at pH 3

but then increases, finally exceeding the value found in the more acid solution. The activity of ^{95g}Tc is found as cationic, uncharged and anionic forms. The cation is preponderant in the unretained fraction at low pH. The proportions of ^{95g}Tc and ^{95m}Tc in the different electrophoretically separated fractions are shown in Figure 3, for a solution of Li^{95m}Tc/⁹⁹TcO₄ at pH 3. Data for solutions at

Table 1. Influence of pH on the chemical distribution of ^{95g}Tc in NH_4TcO_4 solution*

System No	pH	$^{95g}\text{TcO}_4^-$ %	uncharged species %	cation %	anion %
1	0.1	86.3 ± 2.8	3.9 ± 1.7	2.4 ± 0.8	7.4 ± 1.8
2	1.7	55.4 ± 3.0	12.2 ± 2.2	15.2 ± 1.2	17.1 ± 2.2
3	3	34.6 ± 3.9	30.1 ± 3.3	18.7 ± 1.6	16.5 ± 1.8
4	5	54.1 ± 3.9	25.4 ± 0.9	4.5 ± 0.9	15.9 ± 4.0
5	6	70.9 ± 3.1	17.3 ± 2.0	5.4 ± 4.0	6.4 ± 3.1
6	8	85.9 ± 3.4	9.0 ± 1.1	0.9 ± 0.1	4.2 ± 2.0

* 5 parallel experiments

pH 0.1 and pH 6 agree and show that no significant proportion of ^{95m}Tc or ^{99}Tc appears in fractions other than TcO_4^- . These results show that no macroscopic self-radiolysis of the solutions takes place.

The effect of pH on the stabilisation of ^{95g}Tc in NH_4TcO_4 solution is given in Table 1. Not unexpectedly the results are substantially the same as for the solutions of the lithium salt (Figs. 2 and 4).

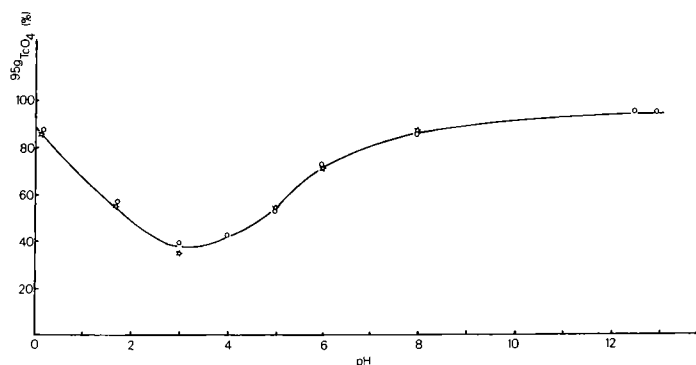
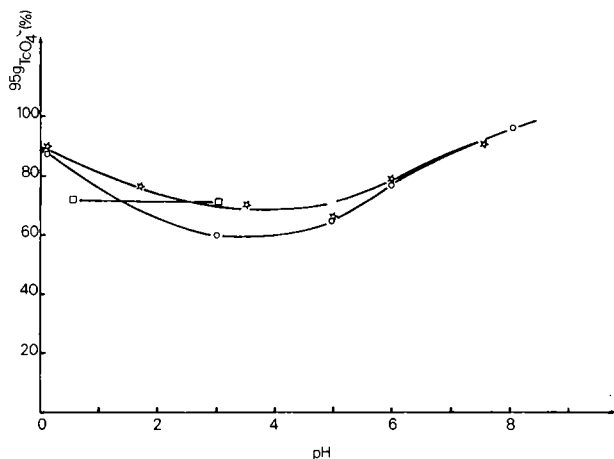
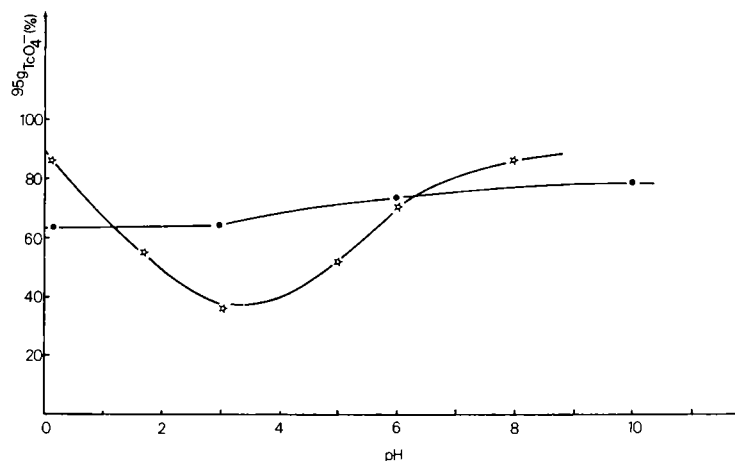
Comparison of results obtained by the electrophoresis and extraction procedures shows extraction leads to higher values for the $^{95g}\text{TcO}_4^-$ fraction; but adding the yields of the uncharged species and the $^{95g}\text{TcO}_4^-$ obtained by electrophoresis gives the retention measured by extraction. Finally,

the results obtained by extraction are similar to those obtained by electrophoresis of the solution in the absence of Tc(IV) carrier.

The effect of pH on the yield of $^{95g}\text{TcO}_4^-$ in KTcO_4 solution is shown in Figure 5. Although the form of the pH dependence is the same as for the lithium and ammonium salts, the minimum R_0 is much higher ($\sim 60\%$ rather than $\sim 40\%$). In view of the dilute solutions used this is a surprising result but it has been confirmed in several independent experiments, even to the extent of using ^{95m}Tc from 3 different irradiations.

Finally, a few experiments have been made in which the solution contained different radical scavengers. A solution of KTcO_4 in CCl_3COOH and NaNO_3 at different concentrations (4 M) and pH (pH = 2.5 for CCl_3COOH and pH = 5 for NaNO_3) gave a $^{95g}\text{TcO}_4^-$ retention higher than 90%. Saturation of the solution with N_2O also gave rather higher retentions in the pH range 1–4. A solution of KTcO_4 containing 80% of alcohol gave a practically constant retention, lower at pH 0.5 and higher at pH 3 than the corresponding aqueous solution. The cationic form practically disappears in these solutions.

No pH-dependence is found for solid samples of potassium pertechnetate. The percentages of the cationic, uncharged and anionic species remain constant at 14%, 10% and 6% respectively. A small increase in retention for solid ammonium pertechnetate may occur at higher pH (Fig. 6).

Fig. 4. Yield of $^{95g}\text{TcO}_4^-$ vs. pH in LiTcO_4 \circ and in NH_4TcO_4 \star . Carrier as for Fig. 2Fig. 5. Yield of $^{95g}\text{TcO}_4^-$ vs. pH in KTcO_4 solution. \circ solution with N_2 , \star solution with N_2O , \square solution containing alcohol. Carrier as for Fig. 2Fig. 6. Yield of $^{95g}\text{TcO}_4^-$ vs. pH in NH_4TcO_4 ; \star aqueous solution, \bullet solid matrix. Carrier as for Fig. 2

4. Discussion

The products of the isomeric transition in aqueous solution appear to be the same as those found after decay in the solid pertechnetates, followed by dissolution for electrophoretic analysis. The sensitivity of the products to oxidation suggests that they are Tc(IV) derivatives; the uncharged species may be $\text{TcO}(\text{OH})_2$, or a related species such as $\text{TcO}(\text{OH})(\text{CH}_3\text{COO})$ [7]. The cationic species may be $\text{TcO}(\text{OH})^+$ [8, 9]. In addition to the TcO_4^- , a small amount of another anionic species was generally found.

Although it is hoped that the use of the Tc(IV) carrier solutions has suppressed extraneous oxidation of products, the retention as TcO_4^- should probably be regarded as a maximum value. However, as the comparison of the two carriers in Figure 1 shows, the pH effect on the distribution of products may not be much affected by the oxidation. The difference between the two Tc(IV) carrier solutions, the acetate containing solution surviving at much higher pH, must be attributed to an acetate complexing of the Tc(IV), stabilizing this oxidation state, so that $\text{TcO}_2 \times n\text{H}_2\text{O}$ precipitation only occurs at a higher pH. Thus the retention was a somewhat lower when this carrier was used, because oxidation of the Tc(IV) becomes a little more difficult. A similar effect was reported in hydrolysed TcCl_6^{2-} solution [7].

In view of the absence of a pH effect on the ^{95g}Tc distribution following the dissolution of the solid potassium salt, after growth of the ground state in the crystals, the pH-dependent distribution found after growth in solution, can only arise from two possible causes:

- (i) The primary ^{95g}Tc species participate in a pH-dependent hot reaction with water.
- (ii) The ^{95g}Tc species are involved in pH-dependent thermal reaction with the not very distant radiolysis products arising from the Auger electrons.

The excitation of the ^{95m}Tc is 38.9 keV, so that the initial conversion electrons will carry about 18 keV for conversion in the K shell (~95%), 36.2 keV for conversion in the L shell (~5%) and 38.4 keV for conversion in M shell (trace) [10]. But the conversion will be followed by an Auger cascade arising from the vacancy so produced. Now the average binding energies of the electrons in the K, L and M shells for technetium are about 21, 2.8 and < 0.5 keV and the fluorescence yield for the filling of the K vacancy is 77%. It will be much lower for subsequent steps. Hence of the total number of electrons emitted in each event (on average perhaps about 5) one, and in about 23% of the events a second electron, has an energy exceeding 10 keV. The remaining three or four electrons will carry 2 keV or less, so that in general there will be a

localised radiolysis of the aqueous medium in the close vicinity of the nascent ^{95g}Tc .

It should be possible to test this latter possibility (ii) by the introduction of scavengers. Our preliminary results looking for OH-scavenging by alcohol and electron scavenging by N_2O , trichloroacetate, or nitrate, where the first of these led to a reduced retention as TcO_4^- at low pH, while the others gave rather higher retentions over the middle range of pH values, seems to suggest that oxidation by the radiolytic hydroxyl might be involved.

It is seen that under all conditions at least 40% of the TcO_4^- ions either survive the isomeric transition, or are reformed so quickly that we cannot interfere with the process. Although the K fluorescence yield is rather high, the majority of Tc atoms undergoing the transition will suffer considerable charging. If this generally leads to a Coulombic explosion, there must be an equally efficient reaction reconverting a large part of the ^{95g}Tc to the TcO_4^- state.

Attention should be drawn to the difference between these results and the well known pH dependence of the (n, γ) retention in the permanganate system. In the latter case a pH effect is found both in solution and dissolution of the irradiated crystals [11, 12]; it has been shown to be due to a pH dependence of the chemical behaviour of Mn^{2+} in the solution [13, 14].

References

1. IANOVICI, E., LERCH, P., PROSO, Z., MADDOCK, A. G.: *Radiochimica Acta* in press.
2. HILLMAN, M., WEISS, A. J.: *Radiochimica Acta* **15**, 79 (1971).
3. DUPLATRE, G.: Thèse CNRS A. O. 11639 (1975).
4. GLENWORTH, P., WRIGHT, C. L.: *J. Inorg. Nucl. Chem.* **31**, 1263 (1969).
5. SCHWEITZER, G. K., WILHELM, D. L.: *J. Inorg. Nucl. Chem.* **3**, 1 (1956).
6. IANOVICI, E., LERCH, P., PROSO, Z., DECOMBAZ, M., MADDOCK, A. G.: *Radiochim. Acta* **26**, 141 (1979).
7. IANOVICI, E., LERCH, P., PROSO, Z., MADDOCK, A. G.: *J. Radioanal. Chem.* **46**, 11 (1978).
8. GORSKI, B., KOCH, H.: *J. Inorg. Nucl. Chem.* **31**, 3565 (1969).
9. OWUNWANNE, A., MARINSKY, J., BLAU MONTE: *J. Nucl. Med.* **18**, 1099 (1977).
10. AGEEV, V. A., GAVRILYUK, V. I., KURYASHKIN, V. T., LATYSHEV, G. D., LYUTYI, I. N., MAKOVETSKII, YU. V., FEOKTISTOV, A. I.: *Bull. Acad. Sci. U. S. S. R. Phys. Ser. (Eng. Trans.)* **33**, 1183 (1969).
11. LIBBY, W. F.: *J. Amer. Chem. Soc.* **62**, 1930 (1940).
12. APERS, D. J., HARBOTTLE, G.: *Radiochimica Acta* **1**, 188 (1963).
13. COGNEAU, M. A., APERS, D. J., CAPRON, P. C.: *Radiochimica Acta* **8**, 143 (1967).
14. COGNEAU, M. A., APERS, D. J., CAPRON, P. C.: *Radiochimica Acta* **10**, 170 (1968).